Aluminum cycling in a tropical montane forest ecosystem in southern Ecuador

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Abstract

Growth limitation induced by Al toxicity is believed to commonly occur in tropical forests, although a direct proof is frequently lacking. To test for the general assumption of Al toxicity, Al, Ca, and Mg concentrations in precipitation, throughfall, stemflow, organic layer leachate, mineral soil solutions, stream water, and the leaves of 17 native tree species were analyzed. We calculated Al fluxes, analyzed temporal trends and modeled Al speciation in the litter leachate and mineral soil solutions. We assessed potential Al toxicity based on soil base saturation, Al concentrations, Ca:Al and Mg:Al molar ratios and Al speciation in soil solution as well as Al concentrations and Ca:Al and Mg:Al molar ratios in tree leaves. High Al fluxes in litterfall (8.77±1.3 to 14.2±1.9 kg ha^{-1} yr^{-1}, mean±SE) indicate a high Al circulation through the ecosystem. The fraction of exchangeable and potentially plant-available Al in mineral soils was high, being a likely reason for a low root length density in the mineral soil. However, Al concentrations in all solutions were consistently below critical values and Ca:Al molar and the Ca^{2+}:$Al_{inorganic}$ molar ratios in the organic layer leachate and soil solutions were above 1, the suggested threshold for

Al toxicity. Except for two Al-accumulating and one non-accumulating tree species, the Ca:Al molar ratios in tree leaves were above the Al toxicity threshold of 12.5. Our results demonstrate a high Al cycling through the vegetation partly because of the presence of some Al accumulator plants. However, there was little indication of an Al toxicity risk in soil and of acute Al toxicity in plants likely reflecting that tree species are well adapted to the environmental conditions at our study site and thus hardly prone to Al toxicity.

Keywords

tropical forest ecosystems, aluminum fluxes, aluminum toxicity, Al speciation, molar Ca:Al ratios

1 Introduction

Many plant species are sensitive to high concentrations of the phytotoxic Al^{3+}, $AlOH^{2+}$, or $AlOH_2^+$ and various other inorganic Al complexes which can occur in soil solutions at pH values < 5.5 (Alleoni et al., 2010; Delhaize and Ryan, 1995; Kabata-Pendias and Pendias, 2001; Macdonald and Martin, 1988). Aluminum phytotoxicity contributes to forest decline in temperate forests (Cronan, 1989; Farr et al., 2009; Godbold et al., 1988). In tropical montane forests, pH usually ranges betwen 4 and 5 and Al toxicity was suggested to contribute to low biomass production and slow nutrient-cycling rates (Bruijnzeel, 2001; Bruijnzeel and Veneklaas, 1998; Hafkenscheid, 2000).

The Al fluxes in an ecosystem vary strongly depending on tree species (coniferous, deciduous), the climate conditions (temperate, tropical) and soil properties like texture, organic C concentrations and pH (Table 1). Aluminum inputs depend on dust deposition and amount of precipitation. Our literature review revealed that the highest Al fluxes with litterfall occur in tropical environments while the highest Al fluxes in soil solution were reported in acidified temperate forests, because of locally low soil pH (Table 1).

The pH is the most important control of Al concentrations in soil solution and acid deposition is a main driver of Al fluxes in a forest (Mulder, 1988). Thus, seasonal acid deposition originating from Amazonian forest fires (Boy et al., 2008a) and the increasing NH_4^+ deposition with subsequent nitrification already in the forest canopy and nitrate leaching through the ecosystem resulted in acidification of the organic layer leachate at our study site (Wilcke et al., 2013), which will probably also couple back to Al fluxes in the system.

A hydroponic experiment with saplings of three different tree species typical for the south Ecuadorian montane forests has shown that Al toxicity thresholds (EC10 values) are between 126 and 376 μM Al in solution (Rehmus et al., 2014). However, knowledge of Al concentrations in soil solutions alone is not sufficient to judge the threat of Al toxicity, because Al speciation is crucial for toxic effects (Alleoni et al., 2010). If the solid Al pool is limited, which is particularly the case in the organic layer compared to the mineral soil, ligand complexation in the solid and dissolved phases leads to detoxification of Al^{3+}. Several studies demonstrated an alleviation of Al toxicity by the formation of organo-Al complexes with dissolved organic matter in solution (Alleoni et al., 2010; Drabek et al., 2005; Hernandez-Soriano et al., 2013; Vieira et al., 2009) and in the solid organic matter (Álvarez et al., 2012; Eimil-Fraga et al., 2015). At our study site, most nutrients are stored in the thick organic layers (Wilcke et al., 2002) where also 51 to 76 % of the fine root length is located (Soethe et al., 2006). Previous studies showed that depending on dissolved organic matter concentrations, 97 % to almost 100 % of the Al in organic layer solution is organically bound in complexes and nontoxic (Wullaert et al., 2013).

A variety of indices based on chemical composition of the soil solid phase, soil solution, and plant tissue can be used to estimate Al stress of an ecosystem (Álvarez et al., 2005). One commonly used approach to estimate the threat of Al stress to plants is the Ca:Al molar ratio in plant tissue and soil solution and the base saturation of the soil (Cronan and Grigal, 1995), because the Ca-Al antagonism may disturb the Ca nutrition at high Al concentrations (Rengel, 1992). According to Cronan and Grigal (1995), indices for a 50 % risk of adverse impacts on tree growth induced by Al stress are a Ca^{2+}:$Al_{inorganic}$ (sum of inorganic Al species) molar ratio of ≤ 1.0 in soil solution, a Ca:Al molar ratio of ≤ 12.5 in the foliar tissue, and a soil base saturation ≤ 15 % of the effective cation-exchange capacity (ECEC). Aluminum can also affect the Mg nutrition of plants (Kidd and Proctor, 2000; Kinraide, 2003). Reduced Mg concentrations in needles of *Picea abies* (L.) H.Karst. in an in-situ experiment with elevated Al concentrations (up to 500 μM) in soil solution were revealed by De Wit et al. (2010). In a previous hydroponic experiment, impaired Mg translocation to the leaves and possibly reduced photosynthesis was suggested as a reason for reduced shoot biomass production under Al stress (Rehmus et al., 2015).

We analyzed Al fluxes and cycling in a tropical mountain forest in southern Ecuador and tested soil, soil solution and plant leaves for indications of Al toxicity to answer the following questions:

1. Is Al cycling enhanced in tropical montane forests because of acid soils and elevated litterfall production?
2. Do toxicity indicators point at negative effects of Al on plant growth?

2 Materials & Methods

2.1 Study site and sampling procedures

The study site is an approx. 9 ha-large microcatchment (MC 2) between 1900 and 2010 m a.s.l. (above sea level) on 30–50° steep slopes on the north-facing part of the Rio San Francisco valley (Boy and Wilcke, 2008). The ecosystem flux measurements in the forest are concentrated along three ca. 20 m-long transects covering about 10 m in elevational difference at 1900 – 1910, 1950 – 1960 and 2000 – 2010 m a.s.l. (MC 2.1, MC 2.2, and MC 2.3, Figure 1). We considered the three measurement transects as replicates to account for the spatial variation in the study catchment.

Incident precipitation and throughfall were collected with Hellmann-type collectors on a clearing and at the three transects in the forest, respectively. Stemflow was collected on five representative large trees in MC 2.1 and surface flow was measured with a V-shaped weir at the outlet of the stream draining MC 2. Further instrumentation (to collect litter leachate, soil solutions, and litterfall) was placed along three measurement transects (MC 2.1 – 2.3). The following equipment was established at each of the three replicate transects: Three litter collectors with the dimension 0.3 m x 0.3 m and 0.5 mm mesh size, three zero-tension lysimeters below the organic layer to collect organic layer leachate from below the Oi, Oe, and Oa horizons (LL), and three suction cups at each of the 0.15 and 0.3 m depths of the mineral soil to collect mineral soil solution (SS15 and SS30, respectively). Weekly sample replicates were bulked to a composite sample per sample type (solution or litterfall) and measurement site prior to chemical characterization. Solution samples were analyzed in weekly resolution while litterfall samples were bulked to monthly samples before chemical analysis. Soil water content was measured with FDR (frequency domain reflectometry) probes at transect MC 2.1 at the 0.1, 0.2, 0.3, and 0.4 m depths. We calculated monthly element concentration means of incident precipitation, throughfall precipitation, stemflow, and surface flow from April 1998 to March 2003, of soil solutions from May 2000 to April 2003, and of the organic layer leachate from April 1998 to December 2007 and September 2009 to April 2010. Our time series included smaller gaps (6 % of time) because of missing samples. Samples of fresh tree leaves representing the most abundant tree species in the highly biodiverse study area (Homeier et al., 2002) were collected in two sampling campaigns between October 2005 and February 2006 and in October 2011 from 21 and 9 individual trees, respectively (17 tree species in total, Table 2). Young leaves were sampled randomly from the tree crown. The base and Al saturation of the effective cation exchange capacities of the mineral soils were determined as the sum of the charge equivalents of Ca, Mg, Na and K or Al, respectively, divided by sum of the charge equivalents of Ca, K, Mg, Na, Mn and Al extracted with 1 M NH_4NO_3 (soil:solution ratio 1:25) from the A horizons of 23 soils. Three of the soil samples were collected at our measurement transects (each composited from three sampling sites, Wilcke et al., 2001), 10 soils were located along an elevational transect near the stream draining the watershed between 1880 and 2100 m a.s.l. (valley bottom) and further 10 soils were located along an elevational transect near the ridge between 1890 and 2110 m a.s.l. (Wilcke et al., 2010). The latter two transects were considered to represent a large part of the soil variation in the study catchment. More detailed information about the study site and sampling is given in the Supporting Material (SM).

2.2 Chemical analyses

Within 24 h of collection of the precipitation, throughfall, stemflow, soil solution, and stream water samples were analyzed first for electric conductivity (EC) (ProfiLine Cond 3110, WTW GmbH, Weilheim, Germany) and then for pH (Sentix HWS, WTW GmbH, Weilheim, Germany), filtered (ashless filters with pore size 4-7 µm, folded filter type 389; Munktell & Filtrak GmbH, Bärenstein, Germany) and frozen at the day of sampling until analysis. To ensure that the time gap between sampling and analysis had no effect on pH, selected samples were analyzed immediately and after 24 and 48 hours and showed no change in pH (Table S1). The samples were kept frozen until further chemical analyses. Aluminum concentrations were determined with inductively-coupled plasma mass spectrometry (ICP-MS, VG PlasmaQuad PG2 Turbo Plus, Thermo

Fisher Scientific, Waltham, USA and 7700x Agilent Technologies, Frankfurt am Main, Germany). The Ca, Mg, K, Na and Al concentrations in leaves and extracts of soils and suspended particulate matter of stream water were analyzed with atomic absorption spectroscopy (AAS, SpectraAA400, Varian, Darmstadt, Germany and Zeenit700P, Analytik Jena, Jena, Germany). Fluoride concentrations were determined with an ion-sensitive electrode (WTW Inolab pH/Ion 735 with a WTW F800 electrode, WTW, Weilheim, Germany) after addition of TISAB III (Fluka Analytical) by standard addition. Concentrations of Cl^- were determined with a Cl^--specific ion electrode (Orion 9617 BN, Thermo Fisher Scientific, Waltham, USA) after adjustment of the ionic strength with a solution of 1.13 g L^{-1} $NaNO_3$+2 mL L^{-1} surfactant (Triton X-100, 50% solution) during the first 3 years on a segmented Continuous Flow Analyzer (CFA, AutoAnalyzer 3 HR, SEAL Analytical, Germany). Concentrations of, NH_4^+, NO_3^-, and PO_4^{3-} were determined photometrically with a CFA (initially a San plus, Skalar, Breda, Netherlands device was used and later the AutoAnalyzer 3 HR). Sulfate was determined by ion chromatography (Dionex ICS-900, Thermo Scientific, Waltham, MA, USA). Total organic carbon (TOC) concentrations were analyzed with a TOC-5050 (Shimadzu, Düsseldorf, Germany).

The litter and leaf samples were digested in a closed vessel microwave system (MARS Xpress, Kamp-Lintfort, Germany and MLS Ethos, Leutkirch, Germany, respectively) after drying and homogenization with an agate ball mill. The litter and leaf samples of 2005/2006 were digested with 65 % HNO_3 and leaf samples of 2011 with 69 % HNO_3/30 % H_2O_2/48 % HF and subsequently with 5 % H_3BO_3 to complex residual HF (16 HNO_3:6 H_2O_2:1 HF:10 H_3BO_3 v/v/v/v). Concentrates of particulate matter in stream water were digested with 65 % HNO_3/48 % HF (4:1 v/v). The quality of digestions and measurements of Al, Ca and Mg concentrations was controlled with the help of the certified reference material (CRM) BCR-100 (beech leaves IRMM, Geel, Belgium). The accuracy of Ca and Al measurement in both types of digests was within ± 5% and that of Mg within ±10% deviation of the certified value. The pH values of the solid soil samples were determined in 0.01 M $CaCl_2$ (soil:solution ratio 1:2.5). The detection limits of our chemical analyses are given in Table S2.

2.3 Calculations and Al speciation modeling

The base saturation and saturation of exchangeable Al was calculated as the proportion of charge equivalent of extractable Ca + K + Mg + Na and Al of the ECEC. The Al fluxes were calculated for 5 consecutive hydrological years from April 1998 to March 2003 (in the case of soil solutions 3 years from May 2000 to April 2003). More details about the calculation of fluxes are given in the supporting material. Surface flow was modeled with the hydrological catchment model TOPMODEL (Beven et al. 1995). Details about the parameterization and validation of the model are given in Fleischbein et al. (2006). Soil water fluxes were calculated from climate data and soil moisture measurements with a soil water budget model as described by Boy et al. (2008b). Data gaps of soil water fluxes (because of lacking soil water contents) were substituted with the help of a regression model of modeled weekly soil water fluxes on measured weekly throughfall volumes (R^2 = 0.85). The Al canopy budget and total Al deposition was estimated with the canopy budget model of Ulrich (1983) assuming Cl^- as inert tracer (Boy and Wilcke, 2008) as described in the SM.

Potential drivers of Al concentrations are soil acidity and concentrations of complexing agents including TOC, F^-, and SO_4^{-2}. Wullaert et al. (2013) showed that only TOC occurred in relevant concentrations for Al complexation. Complexes of other ligands (Cl^-, F^-, NO_3^- , PO_4^{3-} , SO_4^{2-}) hardly contributed to total Al concentrations. Furthermore, total Al concentrations are influenced by dilution/concentration effects which we addressed by including soil moisture contents in our analysis. Multiple regressions were calculated among monthly Al concentrations and Ca:Al molar ratios, respectively, with pH, TOC concentrations and soil moisture (only in the organic layer leachate (see SM for more details).

The Al speciation was calculated using Visual MINTEQ (VMINTEQ, Version 3.0 beta, J.P. Gustafsson) for LL (n=176), SS15 (n=41), and SS30 (n=50) samples, for which a complete data set was available. The F^- concentrations were determined for a subset of 176 samples from all three solution types and were in all cases below the limit of quantification (1.16 μM) and in 89 % of the cases even below the limit of detection (0.37 μM). Thus, for the calculation we set F^- concentrations of all samples to half of the detection limit (0.18 μM). In the model, SO_4^{2-} concentrations were set to 6.35 μM (i.e. the mean sulfate concentration of 31 measured samples of all three solution types). Ionic strength was estimated from EC according to Griffin and Jurinak

(1973). Within VMINTEQ, the NICA-Donnan model was used to assess complexation of Al with humic substances. Details of the NICA-Donnan model are given in Kinniburgh et al. (1996). NICA-Donnan properties of metal complexation by organic acids were taken from the literature (Milne et al., 2003). An active DOM/DOC ratio of 2 was assumed and the dissolved organic acids were adjusted to be 100 % fulvic acids (Tipping and Carter, 2011).

3 Results

3.1 Al fluxes

Mean annual Al fluxes at each of the three measurement transects were lowest in bulk, dry, and throughfall deposition (< 0.6 kg ha^{-1} yr^{-1}, Figure 1). Stemflow contributed negligibly to the Al fluxes reaching the soil (< 0.05 – 5.4 %). Soil deposition by litterfall was 9 to 18 times higher than that of the sum of all dissolved aboveground Al fluxes. The mean annual litter input at MC 2 from April 1998 to March 2003 was 10.0±0.3 t ha^{-1} yr^{-1}. The mean annual canopy budget was positive at each of the three measurement transects. The Al fluxes in organic layer leachate were lower than in mineral soil solutions except at transect MC 2.3, where lowest Al fluxes occurred in SS30. The multiple regression among Al concentrations (C_{Al}) and pH values, soil moisture content, and TOC concentrations (C_{TOC}) in organic layer leachate (Eq. 1) shows the highest partial regression coefficient for the pH, highlighting the importance of pH for Al concentrations in soil solutions (Figure S1).

Eq. 1 $C_{Al} = 7.88 - 0.88 \cdot pH - 0.03 \cdot \text{soil moisture (vol.\%)} + 0.02 \cdot C_{TOC}\ (mgL^{-1})$

$(R^2 = 0.31,\ p < 0.001,\ n = 75)$

The net hydrological export of Al (i.e. SW-BD, Table 1) was slightly negative, indicating a net accumulation of Al, which was even more pronounced when the total catchment budget (i.e. SW-[BD+DD]) was considered. Yet, the loss of Al as suspended particulate matter in stream water averaged 28.8 kg ha^{-1} yr^{-1} (August 2000 – January 2003). From the sum of the net hydrological export and the Al export in suspended particulate matter in stream water, the weathering rate of Al can be estimated as 28.7 kg ha^{-1} yr^{-1} (Likens, 2013). This approach is based on the assumption that the soil thickness is in steady state and that superficial erosion equals soil formation at the subsoil-parent material border (Likens, 2013).

3.2 Al toxicity indicators

The total Al concentrations in LL, SS15 and SS30 were usually higher in mineral soil solutions than in LL (Table 2). The total Al concentrations in precipitation, stemflow and stream water were below 1 μM. The sum of the concentrations of inorganic Al species (Al_{inorg}) in LL, SS15 and SS30 ranged 0.00 - 30.9 μM (Table S3). The fraction of organically bound Al was highest in LL (mean: 96 %) and decreased with soil depth (83 % in SS30).

Aluminum concentrations in leaves of the tree species in the study area were generally in the range of 0.05 – 0.14 (mg g^{-1}, Table 2). Two tree species, *Graffenrieda emarginata* (Ruiz & Pav.) Triana and *Miconia sp*, belonging to the family of Melastomataceae are Al accumulators (Jansen et al., 2002) and therefore had distinctly higher Al concentrations than the Al non-accumulating tree species.

The Ca^{2+}:$Al_{inorganic}$ and Mg^{2+}:$Al_{inorganic}$ molar ratios were distinctly higher in LL than in SS15 and SS30 solutions (Table S3). The Ca and Mg concentrations in the leaves ranged 1.7 – 12.5 and 1.2 – 5.3 (mg g^{-1}), respectively (Table 2). The Ca:Al molar ratios were consistently higher than 12.5 and ranged up to 144. Only the two Melastomataceae species and *Ocotea bentamiana* Mez. (Lauraceae) had Ca:Al molar ratios of 0.5 – 9.2, indicating potential Al toxicity.

The pH in soil A horizons ranged 3.2 – 5.2 (mean 3.7). The base saturation ranged 4.77 – 97.1 % (mean 41.4 %) and the Al saturation ranged 2.65 – 95.2 % (mean 57.7 %). Seven of the 23 soil A horizons had a base saturation of ECEC below 15 % and two soil A horizons had a base saturation between 15 and 16 % (Figure 2). Soils with low base saturation mainly occurred on the ridges (mean±SE base saturation on the ridges: 22.2±5.2 % and in the valley: 65.2±9.1 %) (Wilcke et al., 2010).

4 Discussion

4.1 Al fluxes

The Al fluxes with bulk and dry deposition were well in the range reported from other forests. They were higher than in the Hubbard Brook experimental forest (Likens, 2013) and a humid tropical ecosystem in Fiji (excluding cyclone events, Waterloo et al., 1997), similar to that of a temperate forest in the USA (Rustad and Cronan, 1995, Table 1) but low compared to other tropical rain forests in Brazil (Mayer et al., 2000; Cornu et al., 1998) and a temperate forest in Germany, which was affected by acid deposition (Matzner, 1989; Figure 1 and Table 1). The Al bulk and dry deposition mostly derives from mineral dust, because Al is an ubiquitous element in soils (Macdonald and Martin, 1988), but is also affected by the total amount of precipitation, which is high compared to temperate but medium to low compared to other tropical forests. The positive canopy budget indicates leaching of Al from the canopy. The leaching of cations is a result of proton buffering in the canopy and release of cations to achieve electroneutrality (Matzner, 1989). The lowest Al fluxes occurred in stemflow, which were also lower than in other studies (Figure 1). However, the input of Al and H^+ ions by the stemflow to the soil is restricted to a small area around the stem basis which might have a considerable impact on the local soil chemistry, but minor importance for the total Al fluxes in the ecosystem (Koch and Matzner, 1993; Levia and Frost, 2003).

The Al fluxes with litterfall were high compared to temperate forest ecosystems and most study sites in the tropics (Table 1) and attributable to both, the overall high quantity of litterfall and high Al concentrations in litterfall (Table 2 and Figure 1). Compared with a temperate forest in Bavaria, Germany, mean annual litterfall was two and approximately five times that of a deciduous and a coniferous forest, respectively, while Al concentrations in litterfall were around 10 times higher (Berg and Gerstberger, 2004). Litterfall and associated Al fluxes were lower at some tropical montane forest (Jamaica, Table 1, Hafkenscheid, 2000) but similar to others (Bolivia, Table 1; Gerold, 2008). The Al concentrations in litterfall were three times higher than the Al concentrations in fresh foliage (Table 1), which is in agreement with Hafkenscheid (2000) who reported enriched Al concentrations in litterfall compared to fresh leaves of the same species in a tropical montane forest in Jamaica. They explained the Al enrichment as an attempt of the trees to dispose excess Al via litterfall. Another reason is the withdrawal of mobile essential nutrients prior to leaf fall, which will relatively enrich Al. However, another major explanation for high Al concentrations in leaf litter is the wide distribution of Al-accumulating tree species. The two families Melastomataceae and Rubiaceae, which are known to include Al-accumulating species, belong to the most frequent families and *G. emarginata* is the most frequent tree species in the studied forest (Homeier et al. 2002). However a quantification of the contribution of Al accumulators to Al fluxes in litterfall would require samples in which leaf litter is differentiated according to the species which could not be realized in our study.

The Al fluxes with organic layer leachate and soil solutions had a wide range, covering most of the span reported by other studies from similar soil depths (Figure 1 and Table 1). The Al fluxes with the organic layer leachate and the soil solution are coupled to their pH (Eq. 1). In stream water, the dissolved Al fluxes were low compared to two temperate forest ecosystems in the USA (Likens, 2013; Rustad and Cronan, 1995), which is probably attributable to the high pH of the stream water (Table 3), causing precipitation of Al e.g., as Al hydroxide. However, Al in suspended particulate matter in stream water and thus also the Al weathering rate was 20 times higher than e.g., that of the Hubbard Brook experimental forest (Likens 2013) in line with the more pronounced tropical weathering regime at our study site than at Hubbard Brook.

4.2 Al toxicity indicators

The mean base saturation in the soil A horizons was low and the mean Al saturation high, which implies reduced supply with base cations. The base saturation would even be lower if exchangeable protons had been included to calculate the ECEC as it is done in part of the literature (e.g., Cronan and Schofield, 1990). Because of the higher pH values in the valley bottom soils and lateral addition of leached base metals from above-lying soils, the mean base saturation was significantly higher in the valley bottom than the ridge top soils (Wilcke et al., 2010; Figure 2). The ranges of base and Al saturation are complementary at respective pH values and show that the fraction of exchangeable Al can be high (up to 95 %). In mineral soils, Al might have an indirect negative effect on plant nutrition via Al-P precipitation. However, the soil P status can be improved by chelation of Al in organic complexes (Haynes and Mokolobate, 2001). The resulting nutrient scarcity and high Al concentrations might be the reason for the low root length density in the mineral soils and high root length density in the organic layers (Soethe et al., 2006). Applying the critical base saturation of ≤ 15 % proposed by Cronan and Grigal (1995), out of the 23 analyzed soils in our study approximately 30 % might pose a potential risk of Al toxicity, particularly on the ridges, where 4 of the 7 soils with a BS < 15 % and two soils with marginally higher BS (< 16 %) were located (Figure 2). The percentage of soils with critical base saturation would even increase if exchangeable protons had been included in the ECEC.

The mean pH values in organic layer leachate and soil solutions were consistently < 5.5

and thus favorable for high Al concentrations (Table 3). The total Al concentrations which caused a 10 % reduction in shoot biomass of saplings of three tree species from the same forest (EC10 values: 126 to 376 μM Al, Rehmus et al., 2014) were not approached in any ecosystem solution. To reach the EC10 values, an approximately 8 to 23-fold increase of the mean total Al concentrations in organic layer leachate would be necessary. The lowest Al concentrations at which a negative response of sensitive species was observed ranged from 35 to 170 μM (Schaedle et al., 1989). Thus the present total Al concentrations in the organic layer leachate can be considered as nontoxic. In addition, the Al speciation modeling confirmed that up to 97 % of the Al in the organic layer leachate is organically bound (Table S3). The remaining free Al_{inorg} concentration in the organic layer leachate of approximately 0.5 μM is unproblematic even for Al-sensitive plant species (Wheeler et al., 1992). The mineral soil solutions had higher total Al and lower DOC and thus highest concentrations of inorganic Al species. The mean $Al_{inorganic}$ concentrations were above 0.5 µM in 30 cm depth at transect MC 2.1 and at both soil depths at transects MC2.2 and 2.3 (Table S3) and thus Al toxicity might occur for sensitive plants. However, high $Al_{inorganic}$ concentrations in in the mineral horizons will have a limited Al toxicity effect to local tree species, because 51 to 76 % of the fine root length is concentrated in the organic layer (Soethe et al., 2006). On the other hand, this distribution of root length density may be a reaction to the higher Al concentrations in mineral soil solution compared to organic layer leachate.

Applying the Ca^{2+}:$Al_{inorganic}$ molar ratios in the organic layer leachate and the mineral soil solutions as an indicator for a negative impact on the tree growth (Cronan and Grigal, 1995), only few solutions might pose a 50 % and higher risk of Al stress (Table S3). Because Al has a higher affinity for dissolved organic matter than Ca, the majority of the organic layer leachates and even the mineral soil solutions had a Ca:total Al and even Ca^{2+}:$Al_{inorganic}$ molar ratios far higher than the suggested threshold of 1 (mean Ca^{2+}:$Al_{inorganic}$ molar ratios 1.17 - > 10^{36}, Table S3), which renders an Al effect on plant Ca uptake unlikely. Jorns and Hecht-Buchholz (1985) reported Mg deficiency symptoms in Norway spruce (*P. abies*) at Mg:Al molar ratios of < 0.2. In the hydroponic experiment with species from our study site, Al-induced toxicity symptoms occurred at > 300 μM Al and Mg:total Al molar ratios in nutrient solution were < 0.2 at treatments ≥ 600 μM Al (Rehmus et al., 2014). Thus, Mg deficiency might be a reason for reduced biomass production and Mg:Al molar ratios might be a suitable indicator for Al stress. The Mg:Al molar ratios of SS15 and SS30 were < 0.2 but distinctly higher in all other ecosystem solutions, suggesting problematic Mg:Al molar ratios again only in the mineral soil (Table S2). However, calculating Mg^{2+}:$Al_{inorganic}$ molar ratios resulted in far higher values also in the mineral soil solutions (Table S3).

The Ca concentrations in tree leaves were all in the range required for optimal plant growth (1 – > 50 mg g^{-1}; Marschner, 2012). The Mg concentrations in the leaves (Table 2) are comparable to Mg concentrations in leaves of Brazilian Cerrado trees (0.71 – 2.1 mg g^{-1}; Lilienfein et al., 2001) and in tree leaves of a tropical seasonal rain forest in southwest China (3.2 – 5.4 mg g^{-1}; Shanmughavel et al., 2001). In leaves of 4 and 8 of the 17 analyzed tree species in our study, Mg concentrations were below the limiting values required for optimal growth of crop plants reported by Amberger (1996) (2 – 50 mg g^{-1}) and Marschner (2012) (1.5 – 3.5 mg g^{-1}), respectively. Thus, Mg deficiency might affect growth of some of the tree species. However, low Mg concentrations in trees might primarily result from Mg-poor bedrock and only secondarily from the Mg-Al antagonism. According to Cronan and Grigal (1995), the Ca:Al molar ratios of the two Melastomataceae species and the Lauraceae species which were < 12.5 (Table 2) would mean a 50 % and higher risk of Al stress. However, beneficial effects of Al on plant growth in hydroponic experiments with Al-accumulating tree species, adapted to acid soils, have been reported (Osaki et al. 1997, Watanabe and Okada 2005). Only *O. bentamiana*, which is Al non-accumulating, might suffer immediate Al stress.

5 Conclusions

We conclude that

1. Al fluxes in the ecosystem are mainly controled by high precipitation, biomass production, presence of Al-accumulating plant species and soil pH. Partly high Al fluxes, particularly in litterfall, illustrate a high Al circulation through the ecosystem possibly influenced by the abundance of Al-accumulating plants.
2. The fraction of exchangeable Al on cation exchanger surfaces and the concentrations of dissolved $Al_{inorganic}$ were high in mineral soils. Together with the problematic Mg:Al ratios, Al toxicity is a likely reason for a low root length density in the mineral soil. The concentrations of inorganic Al species in the organic layer leachate were low and most probably below toxicity levels for trees and Ca:Al and Mg:Al molar ratios were

unproblematic. As plants have their main rooting zone in the organic layers, Al toxicity might be of minor importance. The Al concentrations in tree leaves were high in Al-accumulating, but in a normal range for non-accumulating species. The Ca:Al molar ratios in leaves of most Al non-accumulating tree species were unproblematic. Hence, the trees of our study ecosystem seems to be well adapted to the given Al concentrations.

Supplementary Material

More information about the study site, sampling procedures, calculations, one figure and 3 tables can be found in the Supplementary Material.

Acknowledgments

We thank Jürgen Homeier and Ingeborg Haug for their support in determining plant species, Thorsten Peters, Paul Emck, Rütger Rollenbeck, Jörg Bendix, and Michael Richter for providing climate data, Jaime Arturo García Ochoa for providing nutrient concentrations in leaves from the investigated study site, Daniel Kübler for providing maps for the localization of specific tree species in the forest, Alexander Hermann for the illustration of the Al fluxes, the AE Prof. van Groening and three anonymous reviewers for helpful suggestions and comments, which improved the manuscript, Nature and Culture International in Loja, Ecuador, for providing the study area and the research station, Ecuadorian authorities for the research permit, and the German Research Foundation (DFG) for funding (FOR 816, Wi 1601/8-2).

Conflict of interest

The authors declare no competing financial or personal interests.

References

Alleoni, L.R.F., Cambri, M.A., Caires, E.F., Garbuio, F.J., 2010. Acidity and aluminum speciation as affected by surface liming in tropical no-till soils. Soil Sci. Soc. Am. J. 74, 1010–1017.

Álvarez, E., Fernández-Marcos, M.L., Monterroso, C., Fernández-Sanjurjo, M.J., 2005. Application of aluminium toxicity indices to soils under various forest species. For. Ecol. Manage. 211, 227–239.

Álvarez, E., Fernández-Sanjurjo, M.J., Núñez, A., Seco, N., Cort,i G., 2012. Aluminium fractionation and speciation in bulk and rhizosphere of a grass soil amended with mussel shells or lime. Geoderma 173-174, 322–329.

Amberger, A., 1996. Pflanzenernährung, 4th edn. Stuttgart: Ulmer. 319p.

Berg, B., Gerstberger, P., 2004. Element fluxes with litterfall in mature stands of norway spruce and european beech in Bavaria, south Germany. Matzner E, editor. Biogeochemistry of forested catchments in a changing environment. Ecological Studies, vol 172. Berlin Heidelberg, Springer. p271–278.

Bergamini, Scheer, M., Gatti, G., Wisniewski, C., 2011. Nutrient fluxes in litterfall of a secondary successional alluvial rain forest in southern Brazil. Revista de Biologia Tropical 59, 1869–1882.

Beven, K., Lamb, R., Quinn, P., Romanowicz, R., 1995. TOPMODEL. Singh V, editor. Computer models of watershed hydrology. Highlands Ranch, Colorado, Water Resource Publications. p627–668.

Boy, J., Valarezo, C., Wilcke, W., 2008. Water flow paths in soil control element exports in an Andean tropical montane forest. European Journal of Soil Science 59, 1209–1227.

Boy, J., Wilcke, W., 2008. Tropical Andean forest derives calcium and magnesium from Saharan dust. Global Biogeochem. Cycles 22(1), 1–11

Bruijnzeel, L., Veneklaas, E., 1998. Climatic conditions and tropical, montane forest productivity: The fog has not lifted yet. Ecology 79(1): 3–9. DOI 10.2307/176859

Bruijnzeel LA. 2001. Hydrology of tropical montane cloud forests: A reassessment. Water Resour. Res. 1, 1–18.

Cornu, S., Lucas, Y., Ambrosi, J., Desjardins, T., 1998. Transfer of dissolved Al, Fe and Si in two

Amazonian forest environments in Brazil. Eur. J. Soil Sci. 49(3), 377–384.

Cronan, C.S., 1989. Aluminum toxicity in forests exposed to acidic deposition: the Albios results. Water Air Soil Poll. 48, 181–192.

Cronan, C.S., Schofield, C.L., 1990. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and Northern Europe. Environ. Sci. Technol. 24, 1100-1 105

Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. J. Environ. Qual. 24(2), 209–226.

Delhaize, E., Ryan, P.R., 1995. Aluminum toxicity and tolerance in plants. Plant Physiol. 107(2), 315–321. DOI 10.1104/pp.107.2.315

De Wit, H.A., Eldhuset, T.D., Mulder, J., 2010. Dissolved Al reduces Mg uptake in Norway spruce forest: results from a long-term field manipulation experiment in Norway. For. Ecol. Manage. 259(10), 2072–2082.

Dijkstra, F.A. and Fitzhugh, R.D. 2003. Aluminum solubility and mobility in relation to organic carbon in surface soils affected by six tree species of the northeastern United States. Geoderma 114, 33-47.

Drabek, O., Mladkova, L., Boruvka, L., Szakova, J., Nikodem, A., Nemecek, K., 2005. Comparison of water-soluble and exchangeable forms of Al in acid forest soils. J. Inorg. Biochem. 99(9), 1788–1795.

Eimil-Fraga, C., Álvarez-Rodríguez, E., Rodríguez-Soalleiro, R., Fernández-Sanjurjo, M.J., 2015. Influence of parent material on the aluminium fractions in acidic soils under *Pinus pinaster* in Galicia (NW Spain). Geoderma 255-256, 50–57.

Farr, C., Skousen, J., Edwards, P., Connolly, S., Sencindiver, J., 2009. Acid soil indicators in forest soils of the Cherry River Watershed, West Virginia. Environ. Monit. Assess. 158, 343–353.

Fleischbein, K., Wilcke, W., Valarezo, C., Zech, W., Knoblich, K., 2006. Water budgets of three small catchments under montane forest in Ecuador: experimental and modelling approach. Hydrol. Process. 20(12), 2491–2507.

Gerold, G., 2008. The tropical mountain forest – patterns and processes in a biodiversity hotspot. Gradstein SR, Homeier J, Ganser D, editors. Biodiversity and Ecology Series, vol 2.

Göttingen, Universitätsverlag Göttingen. p137–162.

Godbold, D., Fritz, E., Hüttermann, A., 1988. Aluminum toxicity and forest decline. Proc. Nat. Acad. Sci. U. S. A. 85, 3888–3892.

Griffin, B., Jurinak, J.. 1973. Estimation of activity-coefficients from electrical conductivity of natural aquatic systems and soil extracts. Soil Sci. 116(1), 26–30.

Hafkenscheid, R.L., 2000. Hydrology and biogeochemistry of tropical montane rain forests of contrasting stature in the Blue Mountains, Jamaica. Dissertation. Enschede, Print Partners Ipskamp. 315p.

Haynes, R., Mokolobate, M., 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. Nutr. Cycling in Agroecosyst. 59(1), 47–63.

Hernandez-Soriano, M.C., Peña, A., Mingorance, M.D., 2013. Soluble metal pool as affected by soil addition with organic inputs. Environ. Toxicol. Chem. 32(5), 1027–1032.

Hirsch, R.M., Slack, J.R., Smitz, R.A., 1982. Techniques of trend analysis for monthly water quality data. Water Resour. Res. 18: 170–121.

Homeier, J., Dalitz, H., Breckle, S.W., 2002. Waldstruktur und Baumartendiversität im montanen Regenwald der Estación Científica San Franscisco in Südecuador. Bericht der Reinhold-Tüxen Gesellschaft 14, 109–118.

Jansen, S., Watanabe, T., Smets, E., 2002. Aluminium accumulation in leaves of 127 species in Melastomataceae, with comments on the order myrtales. Ann. Bot. 90(1), 53–64.

Jorns, A., Hecht-Buchholz, C., 1985. Aluminiuminduzierter Magnesium- und Calciummangel im Laborversuch bei Fichtensämlingen. Allg. Forstzeitschrift 46, 1248–1252.

Kabata-Pendias, A., Pendias, H., 2001. Trace elements in soils and plants, 3rd edn. Boca Raton: CRC Press. 548p.

Kidd, P.S., Proctor, J., 2000. Effects of aluminium on the growth and mineral composition of *Betula pendula* Roth. J. Experim. Bot. 51(347), 1057–1066.

Kinniburgh, D.G., Milne, C.J., Benedetti, M.F., Pinheiro, J.P., Filius, J., Koopal, L.K., Van Riemsdijk, W.H., 1996. Metal ion binding by humic acid: application of the NICA-Donnan model. Environ. Sci. Technol. 30(5), 1687–1698. .

Kinraide, T.B., 2003. Toxicity factors in acidic forest soils: attempts to evaluate separately the toxic effects of excessive Al^{3+} and H^{+} and insufficient Ca^{2+} and Mg^{2+} upon root elongation. Eur. J. Soil Sci. 54(2), 323–333.

Koch, A., Matzner, E., 1993. Heterogeneity of soil and soil solution chemistry under Norway spruce (*Picea abies* Karst.) and European beech (*Fagus silvatica* L.) as influenced by distance from the stem basis. Plant Soil 151(2), 227–237.

Levia, D.F.J., Frost, E.E., 2003. A review and evaluation of stemflow literature in the hydrologic and biogeochemical cycles of forested and agricultural ecosystems. J. Hydrol. 274(1–4), 1–29.

Likens, G., 2013. Biogeochemistry of a forested ecosystem. New York: Springer-Verlag New York. 159p.

Lilienfein, J., Wilcke, W., Zimmermann, R., Gerstberger, P., Araújo, G.M., Zech, W., 2001. Nutrient storage in soil and biomass of native Brazilian Cerrado. J. Plant Nut. Soil Sci. 164(5), 487–495.

Macdonald, T., Martin, R., 1988. Aluminum ion in biological systems. Trends Biochem. Sci. 13(1), 15–19.

Marschner, P., editor. 2012. Marschner's mineral nutrition of higher plants, 3rd edn. London: Academic Press.

Matzner, E., 1989. Acidic precipitation: Case study Solling. Adriano D, Havas M, editors. Acidic precipitation: Case studies, Advances in environmental science, vol 1. New York, Springer-Verlag New York. p39–83.

Mayer, R., Liess, S., Lopes, M.I.M.S., Kreutzer, K., 2000. Atmospheric pollution in a tropical rain forest: effects of deposition upon biosphere and hydrosphere II. Fluxes of chemicals and element budgets. Water Air Soil Poll. 121(1–4), 79–92.

Milne, C., Kinniburgh, D., Van Riemsdijk, W., Tipping, E., 2003. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. Environ. Sci. Technol. 37(5), 958–971.

Moraes, R.M., Delitti, W.B.C., Struffaldi-De Vuono ,Y., 1999. Litterfall and litter nutrient content in two Brazilian tropical forests. Brazil. J. Bot. 22, 09–16.

Osaki, M., Watanabe, T., Tadano, T., 1997. Beneficial effect of aluminum on growth of plants adapted to low pH soils. J. Soil Sci.Plant Nutr. 43(3), 551–563.

Rehmus, A., Bigalke, M., Valarezo, C., Mora Castillo, J., Wilcke, W., 2014. Aluminum toxicity to tropical montane forest tree seedlings in southern Ecuador: response of biomass and plant morphology to elevated Al concentrations. Plant Soil 382, 301–315.

Rehmus, A., Bigalke, M., Valarezo, C., Mora Castillo, J., Wilcke, W., 2015. Aluminum toxicity to tropical montane forest tree seedlings in southern Ecuador: response of nutrient status to elevated Al concentrations. Plant Soil 388, 87–97.

Rengel, Z., 1992. Role of calcium in aluminium toxicity. New Phytology 121, 499–513.

Rustad, L.E., Cronan, C.S., 1995. Biogeochemical controls on aluminum chemistry in the O horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA. Biogeochem. 29(2), 107–129.

Schaedle, M., Thornton, F., Raynal, D., Tepper, H., 1989. Response of tree seedlings to aluminum. Tree Phys. 5, 337–356.

Shanmughavel, P., Liqing, S., Zheng, Z., Min, C., 2001. Nutrient cycling in a tropical seasonal rain forest of Xishuangbanna, Southwest China. Part 1: tree species: nutrient distribution and uptake. Bioresour. Technol. 80(3), 163–170.

Soethe, N., Lehmann,J., Engels, C., 2006. The vertical pattern of rooting and nutrient uptake at different altitudes of a south Ecuadorian montane forest. Plant Soil 286, 287–299.

Tipping, E., Carter, H.T., 2011. Aluminium speciation in streams and lakes of the UK Acid Waters Monitoring Network, modelled with WHAM. Sci. Tot. Environ. 409, 1550–1558.

Ulrich, B., 1983. Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride. Ulrich B, Pankrath J, editors. Effects of accumulation of air pollutants in forest ecosystems. Dordrecht, D Reidel Publishing. p33–45.

Vieira, F.C.B., Bayer, C., Zanatta, J., Ernani, P.R., 2009. Organic matter kept Al toxicity low in a subtropical no-tillage soil under long-term (21-year) legume-based crop systems and N fertilisation. Austral. J. Soil Res. 47(7), 707–714.

Watanabe, T., Okada, K., 2005. Interactive effects of Al, Ca and other cations on root elongation of rice cultivars under low pH. Ann. Bot.any 95(2), 379–385.

Waterloo, M., Schelleken, J., Bruijnzeel, L., Vugts, H.F., Assenberg, P., Rawaqa, T., 1997. Chemistry of bulk precipitation in southwestern Viti Levu, Fiji. J. Tropic. Ecol. 13, 427–447.

Wheeler, D., Edmeades, D., Christie, R., Gardner, R.. 1992. Effect of aluminum on the growth of

34 plant species: a summary of results obtained in low ionic strength solution culture. Plant Soil 146, 61–66.

Wilcke, W., Yasin, S., Valarezo, C., Zech, W., 2001. Change in water quality during the passage through a tropical montane rain forest in Ecuador. Biogeochem. 55, 45-72.

Wilcke, W., Yasin, S., Abramowski, U., Valarezo, .C, Zech, W., 2002. Nutrient storage and turnover in organic layers under tropical montane rain forest in Ecuador. Eur. J. Soil Sci. 53(1), 15–27.

Wilcke, W., Boy, J., Goller, R., Fleischbein, K., Valarezo, C., Zech, W., 2010. Chapter 43. Effect of topography on soil fertility and water flow in an Ecuadorian lower montane forest. In Bruijnzeel, L.A., F.N. Scatena & L.S. Hamilton (eds.): Tropical Montane Cloud Forests: Science for Conservation and Management. Cambridge University Press, Cambridge, UK, 402-409.

Wullaert, H., Bigalke, M., Homeier, J., Cumbicus, N., Valarezo, C., Wilcke, W., 2013. Short-term response of the Ca cycle of a montane forest in Ecuador to low experimental $CaCl_2$ additions. J. Plant Nutr. Soil Sci. 176(6), 892–903.

Table 1

Aluminum fluxes (kg ha^{-1} yr^{-1}) of bulk (BD) and dry deposition (DD), throughfall (TF), stemflow (SF), litterfall (LF*), organic layer leachate (LL), mineral soil solution (SS**), stream water (SW), and suspended particulate matter loss with stream water (PL) from the literature. * total litterfall (t ha^{-1} yr^{-1}) in parentheses, ** soil depth (m) in parentheses

		Al fluxes (kg ha^{-1} yr^{-1})								
Reference	**Ecosystem**	**BD**	**DD**	**TF**	**SF**	**LF***	**LL**	**SS****	**SW**	**PL**
Current study	tropical montane forest, Ecuador	0.2	0.2	0.5	0.01	11.4 (10.0)	5.0	10.19 (0.15), 6.02 (0.30)	0.18	28.8
Likens (2013)	northern hardwood forest, USA	< 0.01							2.79	1.38
Rustad and Cronan (1995)	northern red spruce forest, USA	0.2		0.06	0.03	0.65	2.1		2.6	
Berg and Gerstberger (2004)	deciduous forest, Germany					0.98 (5.45)				
Matzner et al. (2004)	deciduous forest, Germany							2.4 (0.6)		
Berg and Gerstberger (2004)	coniferous forest, Germany					1.2 (2.14)				
Matzner et al. (2004)	coniferous forest, Germany							17.2 – 26.9 (0.2 – 0.9)		
Matzner (1989)	temperate forest, Germany	1.2	0.9 – 1.3	1.6 – 2.9				17.6 – 52.7 (0.9)		
Cornu et al. (1998)	tropical lowland rainforest, Brazil	1.4		0.6	0.03	2.62		3.7 (0.4)		
Mayer et al. (2000)	rain forest, Brazil	5.2		3.2				26.5 – 43.5 (0.1 – 1)		
Hafkenscheid (2000)	tropical montane forest, Jamaica					1.50 – 5.22 (6.47 – 6.16)	1.9 – 4.9	16.1 – 35.1 (0.05 – 0.14)		
Gerold (2008)	tropical montane forest, Bolivia					15.5 (12.2)				
Bergamini Scheer et al. (2011)	Atlantic rain forest, Brazil					11.2 – 9.69 (6.37 – 3.01)				
Moraes et al. (1999)	Atlantic rain forest, Brazil					5.3 (6.31)				

Table 2

Al, Ca and Mg concentrations and molar Ca:Al ratios in fresh leaves sampled between October 2005 and February 2006 and in October 2011 and in litterfall from April 1998 to March 2003. N is number of individual replicates, values represent mean ± standard error.

Species	Family	N	Ca	Mg (mg g^{-1})	Al	Ca:Al molar ratio
Sampling October 2005 to February 2006						
Purdiaea nutans Planch.	Cyrilliaceae	3	9.8 ± 0.8	2.6 ± 0.3	0.1 ± 0.0	53.7 ± 7.2
Alchornea pearcei Britton.	Euphorbiaceae	3	6.6 ± 1.9	1.9 ± 0.3	0.1 ± 0.0	64.0 ± 16.5
Graffenrieda emarginata (Ruiz & Pav.)	Melastomataceae	3	2.4 ± 0.2	1.6 ± 0.2	3.4 ± 0.4	0.5 ± 0.1
Podocarpus oleifolius (Donex Lamb.)	Podocarpaceae	3	4.3 ± 0.7	1.4 ± 0.2	0.1 ± 0.0	37.1 ± 1.3
Alazatea verticilata (Ruiz & Pav.)	Lythraceae	1	4.7	1.8	0.07	47.9
Clusia ducoides (Engl.)	Clusiaceae	1	10.9	2.0	0.05	144
Hyeronima moritziana (Mull. Arg.)	Euphorbiaceae	1	3.9	1.5	0.09	30.2
Ocotea aciphylla (Nees) Mez.	Lauraceae	1	2.5	1.2	0.1	19.8
Ocotea bentamiana Mez.	Lauraceae	1	1.7	1.2	0.12	9.2
Miconia sp	Melastomataceae	1	7.7	3.3	1.64	3.2
Elaeagia sp	Rubiaceae	1	3.7	1.6	0.10	25.4
Matayba inelegans Spruce ex Radlk.	Sapindaceae	1	3.2	2.7	0.06	34.8
Prunus opaca (Benth.) Walp.	Rosaceae	1	12.5	2.6	0.09	99.0
Sampling October 2011						
Cedrela odorata L.	Meliaceae	1	6.5	2.3	0.10	42.9
Cedrela sp	Meliaceae	2	9.1 ± 2.8	3.3 ± 0.3	0.12 ± 0.02	47.6 ± 9.5
Heliocarpus americanus L.	Tiliaceae	3	7.6 ± 1.4	5.3 ± 0.7	0.14 ± 0.04	42.9 ± 13.3
Tabebuia chrysantha (Jacq.) G. Nicholson	Bignoniaceae	3	5.8 ± 1.3	3.2 ± 0.4	0.07 ± 0.01	53.4 ± 11.5
Litterfall 1998-2003						
litterfall		59	12.1 ± 0.2	4.0 ± 0.1	1.2 ± 0.1	8.5 ± 0.6

Table 3

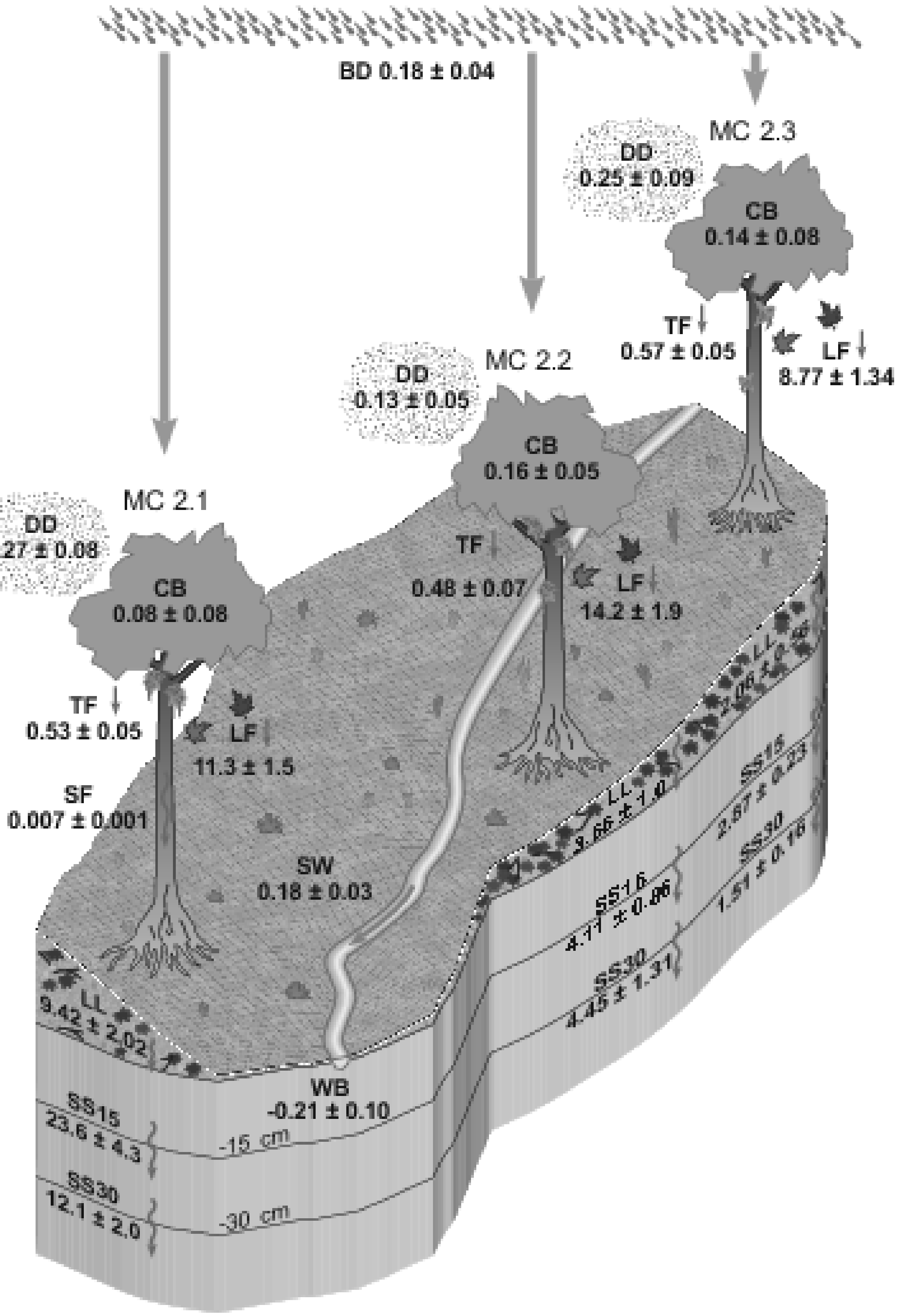
Range and mean of pH, mean (± SE) of Ca, Mg, Al, and TOC concentrations in bulk precipitation, throughfall, stemflow, organic layer leachate (LL), soil solutions in the 0.15 and 0.3 m soil depths (SS15 and SS30, respectively), and stream water at the three measurement transect in Microcatchment 2 (MC2.1 – 2.3) from April 1998 to March 2003 (LL April 1998 to April 2010) and in soil solutions from May 2000 to April 2003.

solution	pH		Ca	Mg	Al	TOC
	range	mean		(μM)		(mg L^{-1})
precipitation MC 2	3.9 – 7.8	5.1	6.44 ± 0.62	4.44 ± 0.47	0.33 ± 0.04	5.28 ± 0.18
throughfall MC 2.1	4.5 – 8.2	6.2	25.1 ± 1.7	20.7 ± 1.3	1.39 ± 0.08	13.5 ± 0.4
throughfall MC 2.2	4.9 – 7.5	6.2	22.9 ± 1.2	20.4 ± 1.1	1.30 ± 0.08	14.3 ± 0.4
throughfall MC 2.3	4.2 – 8.0	6.0	41.9 ± 1.7	43.1 ± 2.0	1.47 ± 0.09	17.4 ± 0.8
stemflow MC 2.1	4.2 – 7.7	6.1	26.3 ± 1.4	22.0 ± 1.2	0.99 ± 0.07	18.3 ± 0.5
stream water MC 2	5.5 – 9.1	6.7	16.6 ± 0.7	18.2 ± 0.6	0.47 ± 0.07	4.48 ± 0.28
LL MC 2.1	3.8 – 6.6	4.4	31.9 ± 1.6	45.5 ± 1.9	27.18 ± 0.8	40.8 ± 0.9
LL MC 2.2	3.6 – 7.5	4.6	48.8 ± 2.5	58.2 ± 3.0	14.3 ± 0.9	33.0 ± 0.9
LL MC 2.3	3.3 – 6.9	5.0	111 ± 5.2	89.7 ± 4.8	4.42 ± 0.36	46.5 ± 1.9
SS15 MC 2.1	3.8 – 4.6	4.2	7.99 ± 1.20	7.14 ± 0.92	73.0 ± 3.02	27.0 ± 0.6
SS15 MC 2.2	4.0 – 5.6	4.4	6.19 ± 0.77	24.3 ± 1.9	12.4 ± 0.94	7.80 ± 0.23
SS15 MC 2.3	4.4 – 5.2	4.9	31.6 ± 1.9	16.6 ± 1.4	9.35 ± 0.32	10.7 ± 0.3
SS30 MC 2.1	4.1 – 4.9	4.4	3.53 ± 0.50	3.70 ± 0.55	36.8 ± 1.9	15.5 ± 0.4
SS30 MC 2.2	4.2 – 5.6	4.5	8.71 ± 1.08	24.7 ± 3.5	13.3 ± 1.4	7.77 ± 0.44
SS30 MC 2.3	4.4 – 5.6	5.2	40.6 ± 11.4	21.2 ± 5.0	4.86 ± 0.28	7.59 ± 0.36

Figure 1. Schematic illustration of Al fluxes (kg ha^{-1} yr^{-1}) in bulk (BD) and dry deposition (DD), throughfall (TF), litterfall (LF), stemflow (SF), organic layer leachate (LL), soil solution in the 0.15 (SS15) and 0.3 (SS30) m soil depths, and stream water (SW), and the Al canopy (CB) and dissolved Al catchment budgets (WB) for an approximately 9-ha large water catchment under tropical montane rain forest in southern Ecuador. Shown are arithmetic means of annual values (± SE) from 1998 to 2003 (n = 5), in case of soil solutions from 2000 to 2003 (n = 3).

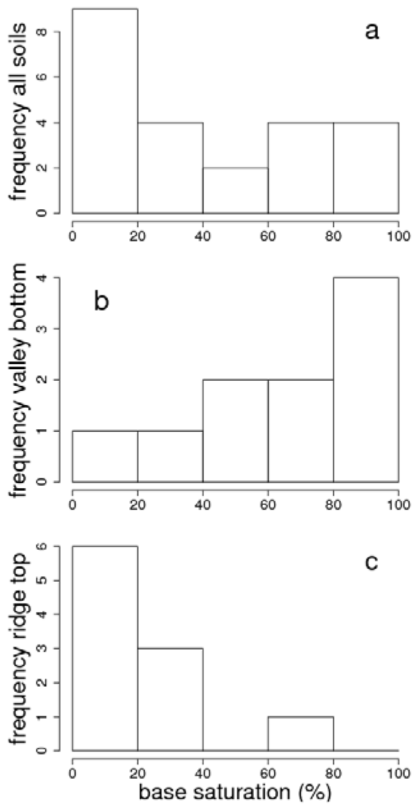
Figure 2. Frequency histogram of base saturation (% of ECEC) of 23 A horizons (a), of selected 10 A horizons in the valley bottom (b), and selected 10 A horizons on the ridge top of a 9-ha large catchment (MC 2).

Figure 1



BD 0.18 ± 0.04
MC 2.1
DD
0.27 ± 0.08
CB
0.08 ± 0.08
TF
0.53 ± 0.05
LF
11.3 ± 1.5
SF
0.007 ± 0.001
SW
0.18 ± 0.03
LL
9.42 ± 2.02
SS15
23.6 ± 4.3
SS30
12.1 ± 2.0
-15 cm
-30 cm
WB
-0.21 ± 0.10
MC 2.2
DD
0.13 ± 0.05
CB
0.16 ± 0.05
TF
0.48 ± 0.07
LF
14.2 ± 1.9
LL
3.66 ± 1.0
SS15
4.11 ± 0.86
SS30
4.45 ± 1.31
MC 2.3
DD
0.25 ± 0.09
CB
0.14 ± 0.08
TF
0.57 ± 0.05
LF
8.77 ± 1.34
LL
2.06 ± 0.46
SS15
2.67 ± 0.23
SS30
1.51 ± 0.16

Figure 2



a
frequency all soils
0
2
4
6
8
0
20
40
60
80
100
b
frequency valley bottom
0
1
2
3
4
0
20
40
60
80
100
c
frequency ridge top
0
1
2
3
4
5
6
0
20
40
60
80
100
base saturation (%)